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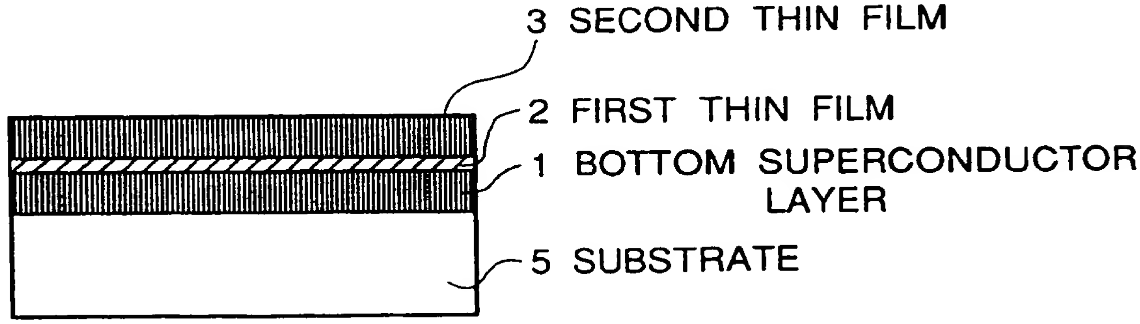
(54) Process for preparing layered thin films.

(57) A process for depositing successively a plurality of thin films on a bottom superconductor layer made of oxide superconductor deposited on a substrate in a single chamber successively preferably under one of two conditions : in a first condition, deposition of a first thin film to be deposited directly on the bottom super-conductor layer is effected under-such condition that the bottom superconductor layer is heated above the oxygen-trap temperature (T_{trap}) at which oxygen enter into the oxide superconductor but lower than a film forming temperature of the bottom superconductor layer, and in a second condition, the bottom superconductor layer is heated in ultra-high vacuum at a temperature which is lower that said oxygen-trap temperature (T_{trap}) but higher than a temperature which is lower by 100 °C than the oxygen-trap temperature (T_{trap} - 100 °C) and then the first thin film is deposited thereon.

FIGURE 1D



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An object of the present invention is to solve the problems and to provide a process for preparing layered thin films comprising a bottom superconductor layer and the other thin film layers deposited on the bottom superconductor layer and having improved crystallinity and continuity especially at superconducting interfaces.

Summary of the Invention

The present invention provides a process for depositing successively a plurality of thin films on a bottom superconductor layer made of oxide superconductor deposited on a substrate, characterized in that deposition of all of the bottom superconductor layer and the thin films is carried out in a single chamber successively.

The deposition is carried out preferably under one of following conditions (1) and (2):

(1) Deposition of a first thin film to be deposited directly on the bottom superconductor layer is effected under such condition that the bottom superconductor layer is heated above the oxygen-trap temperature (T_{trap}) at which oxygen enter into the oxide superconductor but lower than the film forming temperature of the bottom superconductor layer.

(2) The bottom superconductor layer is heated in a ultra-high vacuum chamber at a temperature lower than the oxygen-trap temperature (T_{trap}) but higher than a temperature which is lower by 100 °C than the oxygen-trap temperature (T_{trap} - 100 °C), and then the first thin film is deposited on the bottom superconductor layer.

The oxygen-trap temperature (T_{trap}) and the film forming temperature are known for respective oxide superconductor.

The process according to the present invention is applicable to any known oxide superconductors and is advantageously applicable to Y-Ba-Cu-O oxide superconductor. Bi-Sr-Ca-Cu-O oxide superconductor and Tl-Ba-Ca-Cu-O oxide superconductor which have the most attractive properties including their high critical temperatures.

The substrate is preferably a single crystal of oxide such as MgO, $StTiO_3$, $PrGaO_3$ or the like.

According to the present invention, a layered structure containing at least one thin film of oxide superconductor of high quality can be produced under one of the conditions (1) and (2).

Preferably, in both conditions (1) and (2), deposition of the bottom and top superconductor layers and an oxygen-containing thin film to be deposited on the bottom superconductor layer is carried out in an atmosphere of oxygen having the purity of higher than 5 N (99.999%). Existence of H_2O and CO_2 in oxygen deteriorate the oxide, superconductor because they react easily with the oxide superconductor so that H_2O and CO_2 should be eliminated as small as possible.

In a preferred embodiment, the bottom superconductor layer is a c-axis oriented thin film of $Y_1Ba_2Cu_3O_{7-x}$, the first thin film is made of non-superconductor, for example oxide such as MgO or metal such as Ag and a second thin film to be deposited on the first thin film is a top superconductor layer of $Y_1Ba_2Cu_3O_{7-x}$. In this preferred embodiment, deposition of all thin films to be deposited on the bottom superconductor layer is effected at a substrate temperature between 400 and 600 °C under the deposition of condition (1), and the bottom superconductor layer is heated in ultra-high vacuum of lower than 1×10^{-9} Torr at the substrate temperature between 350 and 400 °C before the first thin film is deposited under the condition (2).

When deposition of the first thin film is carried out in the temperature range defined by the condition (1), enough oxygen enter into the oxide superconductor and diffusion of constituent elements of the first thin film into the bottom superconductor layer can be prevented effectively. For example, when the bottom superconductor layer is a thin film of Y-Ba-Cu-O oxide superconductor, the first thin film of MgO or Ag is deposited at the substrate temperature between 400 and 600 °C.

When deposition of the first thin film is carried out in the temperature range defined by the condition (2), oxygen do not escape out of the bottom superconductor layer and constituent elements of the thin film deposited directly on the bottom superconductor layer do not diffuse or migrate into the the bottom superconductor layer. For example, when the bottom superconductor layer is a thin film of Y-Ba-Cu-O oxide superconductor, the first thin film of MgO or Ag is deposited at the substrate temperature between 350 and 400 °C.

In both conditions (1) and (2), all thin films to be deposited on the bottom superconductor layer should not be deposited above the film forming temperature at which the bottom superconductor layer has been deposited.

The process according to the present invention characterized by the condition (1) and (2) is useful for fabricating a superconducting element comprising a bottom superconductor layer, an intermediate layer made of insulator or ordinary conductor and a top superconductor layer having a different crystal orientation.

In the process according to the present invention, all layers of bottom superconductor layer and thin films deposited thereon must be produced successively in a single chamber so that the bottom superconductor layer does not contact with air and hence a surface of the bottom superconductor layer is neither contaminated nor deteriorated by a reaction with moisture in air.

Atmosphere	Ar	:	90 %
	O_2	:	10 %
Pressure		:	10 Pa

Then, a thin film or oxide superconductor of $Y_1Ba_2Cu_3O_{7-x}$ (3) having a thickness of 200 nm is deposited on the resulting thin film of MgO (2). Deposition of this top superconductor layer (3) can be carried out by the same method :as above but the substrate temperature must be adjusted in a range between 400 and 600 °C. The off-axis sputtering is carried out under following operational conditions:

Sputtering gas	Ar	:	90 %
	O_2	:	10 %
Pressure		:	10 Pa
Substrate temperature		:	570 °C

All procedures are carried out in a single chamber successively. It is confirmed that three layers prepared by the process according to the present invention possess improved crystallinity and continuity especially at superconducting interfaces.

Example 2 (Condition 1)

Example 1 is repeated but the MgO thin film is replaced by a thin film of Ag of the same thickness.

In this Example 2, after deposition complete, the substrate temperature is lowered to 500 °C and then a thin film of Ag is deposited up to a thickness of 10 nm without oxygen by evaporation method under following conditions:

Atmosphere Ar : 100 %
Pressure : 10 Pa

Then, the substrate temperature is adjusted at 570 °C and a second thin film of oxide superconductor of $Y_1Ba_2Cu_3O_{7-x}$ (3) having a thickness of 200 nm is deposited on the resulting thin film of Ag by off-axis sputt ring under the same operational conditions as Example 1.

All procedures are carried out in a single chamber successively. It is confirmed that three layers prepared by the process according to the present invention possess improved crystallinity and continuity especially at superconducting interfaces.

Example 3 (Condition 2)

In this Example 3 also, three-layered thin films of a bottom superconductor layer of $Y_1Ba_2Cu_3O_{7-x}$, an intermediate MgO layer and a top superconductor layer of $Y_1Ba_2Cu_3O_{7-x}$ are deposited successively on a substrate of MgO(100) by the condition (2) of the process according to the present invention whose steps are illustrated in Fig. 1.

At first, a substrate (5) of MgO (100) is placed in a ultra-high vacuum chamber which is then evacuated to 1×10^{-9} Torr.

Then, high pure oxygen having a purity of 99.999 % and argon gas are introduced in the ultra-high vacuum chamber and a thin film of c-axis oriented thin film of oxide superconductor of $Y_1Ba_2Cu_3O_{7-x}$ (1) having a thickness of 300 nm is deposited on the substrate (5) of MgO (100) by off-axis sputtering method under following operational conditions(Fig. 1B):

oxide superconductor deposited on a substrate, characterized in that deposition of said thin films is carried out in a single chamber successively.

2. The process set forth in claim 1 wherein deposition of a first thin film to be deposited directly on said bottom superconductor layer is effected under such condition that said bottom superconductor layer is heated above the oxygen-trap temperature (T_{trap}) at which oxygen enter into said oxide superconductor but lower than a film forming temperature of said bottom superconductor layer.

3. The process set forth in claim 1 or 2 wherein deposition of said bottom superconductor layer is carried out in an atmosphere of oxygen having the purity of higher than 5 N (99.999%).

4. The process set forth in any one of claim 1 to 3 wherein deposition of oxygen-containing thin films to be deposited also is carried out in an atmosphere of oxygen having the purity of higher than 5 N (99.999%).

5. The process set forth in any one of claim 1 to 4 wherein said bottom superconductor layer is a c-axis oriented thin film of $Y_1Ba_2Cu_3O_{7-x}$.

6. The process set forth in claim 5 wherein deposition of all thin films to be deposited is effected at a temperature of said bottom superconductor layer between 400 and 600 °C.

7. The process set forth in any one of claim 1 to 6 wherein said first thin film is made of non-superconductor.

8. The process set forth in claim 7 wherein said non-superconductor is oxide such as MgO or metal such as Ag.

9. The process set forth in any one of claim 1 to 8 wherein a second thin film to be deposited on said first thin film is a top superconductor layer of $Y_1Ba_2Cu_3O_{7-x}$.

10. The process set forth in any one of claim 1 to 9 wherein said substrate is a single crystal.

11. The process set forth in claim 1 wherein said bottom superconductor layer is heated in ultra-high vacuum at a temperature which is lower than said oxygen-trap temperature (T_{trap}) but higher than a temperature which is lower by 100 °C than said oxygen-trap temperature (T_{trap} - 100 °C), and then said first thin film is deposited on said bottom superconductor layer.

12. The process set forth in claim 11 wherein said bottom superconductor layer is heated in ultra-high vacuum of lower than 1×10^{-9} Torr.

13. The process set forth in claim 11 or 12 wherein said bottom superconductor layer is a c-axis oriented thin film of $Y_1Ba_2Cu_3O_{7-x}$.

14. The process set forth in claim 13 wherein said first thin film is deposited on said bottom superconductor layer after the temperature of said bottom superconductor layer is adjusted between 350 and 400 °C.

15. The process set forth in any one of claim 11 to 14 wherein said first thin film is made of non-superconductor.

16. The process set forth in claim 15 wherein said non-superconductor is oxide such as MgO or metal such as Ag.

17. The process set forth in any one of claim 11 to 16 wherein a second thin film to be deposited on said first thin film is a top superconductor layer of $Y_1Ba_2Cu_3O_{7-x}$.

18. The process set forth in any one of claim 11 to 17 wherein wherein deposition of said bottom superconductor layer is carried out in an atmosphere of oxygen having the purity of higher than 5 N (99.999%).

19. The process set forth in any one of claim 11 to 18 wherein deposition of oxygen-containing thin films to b deposited also are carried out in an atmosphere of oxygen having the purity of higher than 5 N (99.999%).

20. The process set forth in any one of claim 11 to 19 wherein said substrate is a single crystal.

FIGURE 1A

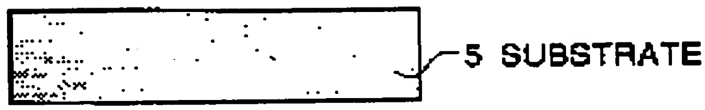

FIGURE 1B

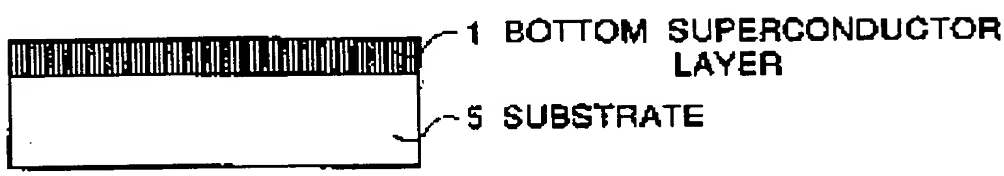

FIGURE 1C

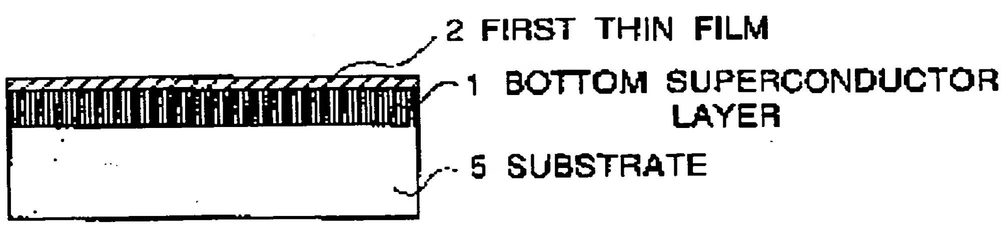

FIGURE 1D